Total Synthesis of (of (-)-Daphnezomines A and B
Xu, G.; Wu, J.; Li, L.; Lu, Y.; Li, C.*

*J. Am. Chem. Soc. 2020, 142, 15240-15245.

1) H₂, Rh/Alumina then TIPSOTf, Et₃N
2) Se, Chloramine-T
3) allyl bromide, NaH
4) Pd(OAc)₂, O₂
5) 1, p-TsOH
6) 9-BBN, then 2, Pd(dppf)Cl₂ aq. NaOH, AsPh₃
7) TFA, then aq. NaOH
8) LaCl₃•2LiCl, 3
9) Na, naphthalene then Boc₂O, Et₃N, then DMP
10) Burgess reagent

What is the name of the starting material?
(S)-(+)−carvone

Step 2: Name the reagent and propose a mechanism
- Sharpless aminating reagent

Step 4: Propose a mechanism
hint: another ring forms
- an oxo-π-allylpalladium species is formed as intermediate, which inserts into the alkene followed by a β-H elimination. Good way construct a,b-unsaturated cyclic ketones

Step 6: Name of the reaction?
- B-alkyl Suzuki-Miyaura coupling

Step 8: Name of this salt?
- Knochel salt

Step 10: Structure of Burgess reagent?

What is the name of the starting material?
(S)-(+)−carvone

Step 2: Name the reagent and propose a mechanism
- Sharpless aminating reagent

Step 4: Propose a mechanism
hint: another ring forms
- an oxo-π-allylpalladium species is formed as intermediate, which inserts into the alkene followed by a β-H elimination. Good way construct a,b-unsaturated cyclic ketones

Step 6: Name of the reaction?
- B-alkyl Suzuki-Miyaura coupling

Step 8: Name of this salt?
- Knochel salt

Step 10: Structure of Burgess reagent?
Step 11: Name of reagent 4?
- Bobbitt's salt

Step 13: How would you classify this reaction according to Baldwin's rule? What could be a potential competing side reaction? Provide a mechanism
- 6-endo-trig cyclization
- enone reduction by resulting Fe-H
- HAT-mediated radical conjugate addition followed 1,5-proton transfer from ammonium ion. Presence of ammonium ion is necessary.

Step 14: hint - epimerization
Step 2 Mechanism:
Sharpless aminating reagent (modified by Magnus)

Step 4 mechanism

Step 13 mechanism

(acac)$_2$Fe–H

Competing pathway could be Fe-H insertion into enone; desired position is sterically crowded and electronically richer than enone